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THE VAPOR PRESSURES OF ZINC OVER ALUMINUM-ZINC ALLOYS.

(METAL VAPOR PRESSURES II.)¹⁾

By A. Schneider and E. K. Stoll²⁾.

(Communication from the Kaiser-Wilhelm-Institute for Metal Research at Stuttgart.)

a) Experimental method.

For the investigation of the zinc-vapor pressures over aluminum-zinc alloys, we used a method that was basically different from the one that was used in the preceding communication, for the determination of the magnesium-vapor pressures. The method used for this investigation was first described by R. Hargreaves³⁾ and was applied with a few modifications. The method is based on the following principle (Fig. 1):

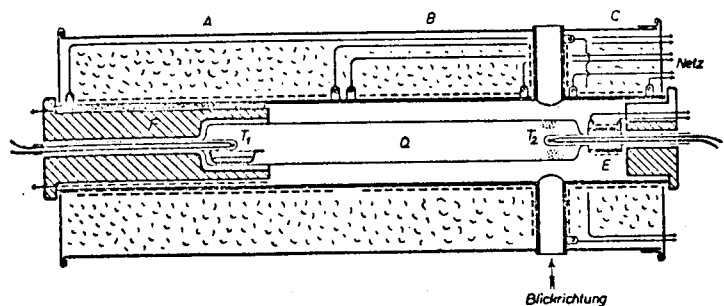


Fig. 1

Arrangement of the oven for vapor pressure measurements, according to Hargreaves.

A quartz tube that is closed in all directions, and at the ends of which we find one quartz tube seal each, for the introduction of a thermometer, is located in a resistance-heated oven. At the beginning of the experiment, the oven which is equipped with various coils (A, B, C) and the total length of which amounts to

1) Metal-vapor pressures I, see the preceding communication.

2) D 93.

3) R. Hargreaves, Journ. Inst. Metals 64, 115 (1939).

60 x 30 cm, is adjusted in such a way that the same temperature will prevail over the entire length of the quartz tube Q. Somewhat later, a zinc-vapor pressure will appear inside the evacuated quartz tube Q. This pressure will correspond to the temperature T_1 of the alloy sample which is located, within a little vessel at exactly the same location. We are using a massive ceramic equalizing body F, with an additional heating coil, to keep this temperature constant. After the adjustment for a zinc-vapor pressure balance above the alloy, a gradually increasing temperature drop will be generated over the entire length of the quartz tube Q, by reducing the temperature in the parts C and B of the oven. This will be continued until such a time as a zinc condensate will form at the point T_2 of the quartz tube. This condensate will be determined by means of a telescopic observation through a horizontal cross hole of the oven (diameter = 10 mm). The temperature of the first appearance of a zinc condensate makes it possible, when the temperature T_1 of the alloy is known, to determine the zinc-vapor pressure provided the concentration is known: the vapor pressure of the pure zinc at a temperature of T_2 is the same as that of the zinc above the alloy at a temperature of T_1 . By switching on the heating coil E, the zinc condensate may again be "chased off," and the temperature of the disappearance of the metallic zinc may be determined. When a steadily increasing temperature drop is generated in a sufficiently slow manner, then it will be possible to determine the temperature of the appearance and of the disappearance of the condensate with a precision of less than $\pm 1^\circ \text{C}$.

Accordingly, the precision of the pressure values can be indicated, within the temperature range under investigation, on the basis of the partial pressures of the pure zinc, at an average of $\pm 2\%$ of the absolute values¹⁾. The vapor pressure

1) The precision of the measuring values is due solely to the temperature coefficient of the zinc-vapor pressure. An error of $\pm 1^\circ \text{C}$ in the determination of the temperature corresponds: at $P_{\text{Zn}} = 0.5 \text{ mm}$ to $\pm 2.7\%$; at $P_{\text{Zn}} = 5 \text{ mm}$ to $\pm 2.2\%$; at $P_{\text{Zn}} = 30 \text{ mm}$ to $\pm 1.7\%$.

values of the pure zinc, that have been used for the evaluation, have been taken from the book of tables by Landolt-Börnstein-Roth-Scheel¹⁾.

b) Measuring results.

The results of the vapor pressure determinations, inasmuch as they concern the zinc-vapor pressures that are in a state of equilibrium, with homogeneous smelting, have been shown in Figs. 2 and 3, for a first survey. Fig. 2 shows the vapor pressure curves for the alloys examined as functions of the temperature; the vapor pressures have been extrapolated up to the boiling points. Fig. 3 clarifies, by isotherms for 650 to 800 centigrades, the approximately rectilinear dependence of the vapor pressures on the composition of the molten mass.

In Figs. 4a and 4b, all experimental results have been compiled in $\log p$ - $1/T$ -diagrams. As long as the alloys remain within the area of one homogeneous molten mass, the individual measuring points are located, with great precision, on one straight line. But, below the liquidus line, the vapor pressure curves present surprising and striking changes of direction. For the interpretation of these findings, we have represented in Fig. 5 two characteristic curves of the alloys with 10 and 30% of zinc, per weight, side by side with the diagram of state of the system Al-Zn. When the liquidus line has been passed, then the molten masses dissociate into a molten mass that is richer in zinc, and into the solid γ -mixed crystal. The consequence thereof is a considerable increase of the zinc-vapor pressure in the heterogeneous area of the molten mass + γ . Below the solidus line, the result will be zinc-vapor pressures that lie on the elongation of the $\log p$ - $1/T$ -straight line, that had been found at higher temperatures for the homogeneous non-dissociated molten mass. The diversity of the inclination of the $\log p$ - $1/T$ -straight

1) Landolt-Börnstein-Roth-Scheel, Physikalischchemische Tabellen, Berlin, 1931, II. Erg.-Bd. p. 1338.

[1 - Vapor pressure of pure zinc (according to Landolt-Börnstein,...)]
 [2 - 85% of zinc per weight, etc.]

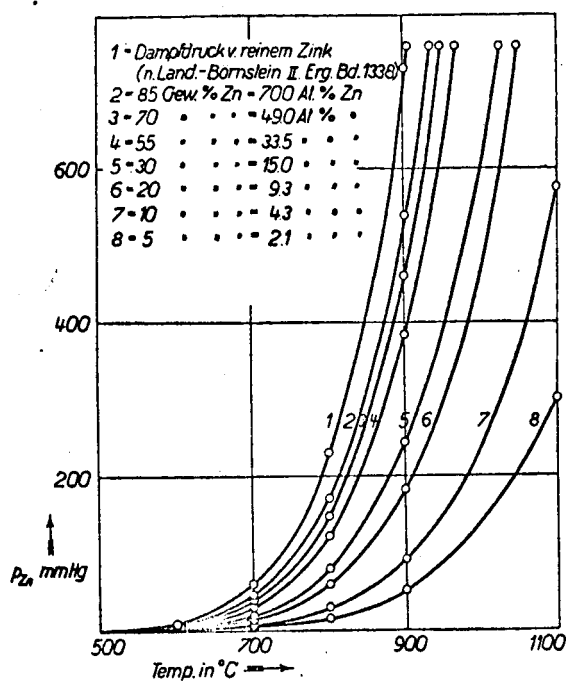


Fig. 2. Vapor pressure curves of molten Al-Zn masses.

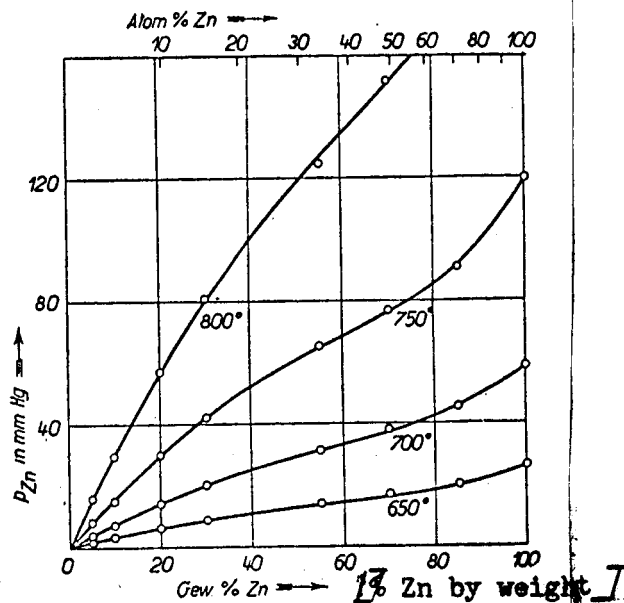


Fig. 3. Al-Zn vapor pressure isotherms.

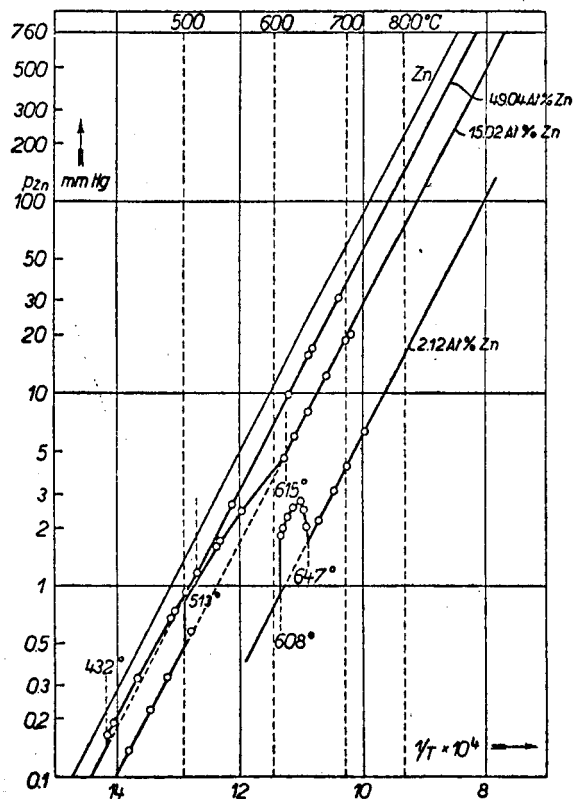


Fig. 4a. log p-1/T diagram for Al-Zn alloys.

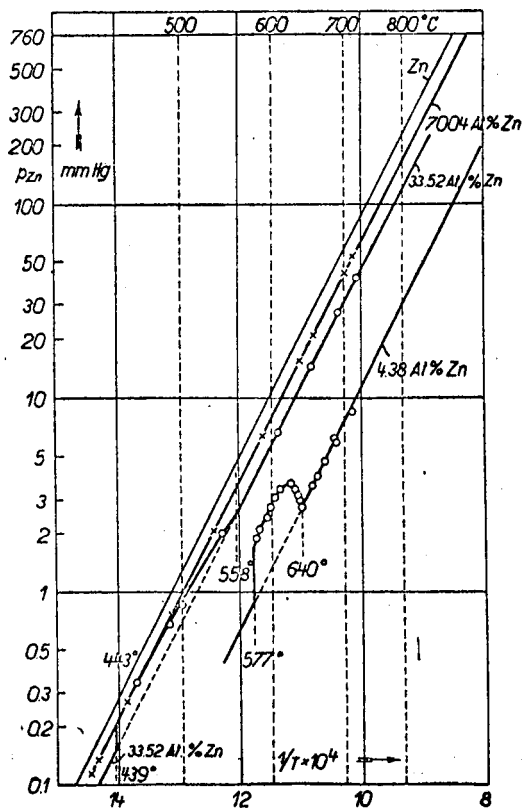


Fig. 4b. log p-1/T diagram for Al-Zn alloys

line for the homogeneous molten mass and the homogeneous mixed crystal, which must be postulated on the basis of the theory, is evidently too small to be noted experimentally by means of this method. Point A in the 30% alloy was measured when the temperature was falling, while point B was measured while the temperature was rising. That means: in the first case, the molten mass was not yet homogenized after chronologically brief passing through the solidus line, while in the second case the solid γ -mixed crystal had not yet become dissociated following the passing through the solidus line. The vapor pressure curve will have to present a sudden change between those two points, at a temperature that lies on the solidus line for the present concentration. When we consider the two vapor pressure curves in Fig. 5, it becomes directly evident that the deviations from the rectilinear course of the $\log p-1/T$ -curve will increase as the Al-contents increase: the curve will pass through a maximum in the case of higher Al-contents, while only a deviation toward higher zinc-vapor pressures can be observed in the case of low Al-contents. The temperatures of the solidus line and liquidus line are to be taken from the pressure curves in the best possible agreement with the diagram of state. This means that the zinc-vapor pressure, with which the molten mass that is richer in zinc and the mixed crystal that is poorer in zinc, are jointly in a state of balance, is evidently determined by the molten mass that is richer in zinc. Since, toward the side of the alloys that are richer in zinc, 1) the liquidus line presents a steeper drop, whereby the percentage of the dissociation is being reduced, and 2) the relative differences of the zinc-vapor pressure above the homogeneous molten mass are decreasing as the zinc contents increase, the magnitude of the dissociation effect will, accordingly, become more and more apparent as the zinc contents are decreasing.

Fig. 6 may serve to explain the dissociation effect¹⁾. In this figure, the

1) Cf. W. Schottky, H. Ulich and C. Wagner, *Thermodynamik*, Berlin 1928, p. 363-367.

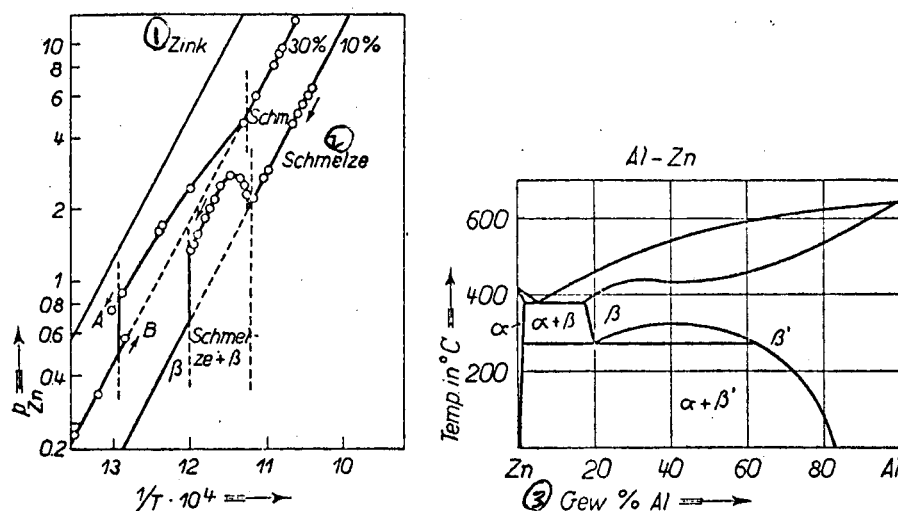


Fig. 5

Vapor pressure curves for Al-Zn.
 [① Zinc; ② Molten mass; ③ % Al per weight.]

part of an activity curve ECS has been shown that is supposed to be valid for the temperature T_3 . We shall assume that, at that temperature, the alloy having an atomic refraction of x is within the area of the homogeneous molten mass. When we cause this alloy to have the temperature of T_2 in the bi-phase region, then the alloy will disassociate into a mixed crystal of the composition y and into a molten mass of the composition z . Let us assume for this case that the activity curves for the temperatures T_3 and T_2 are practically identical, due to a small temperature coefficient of the activity. At the temperature T_2 , the mixed crystal having the composition y and the molten mass having the composition z must be in a state of equilibrium, with the same zinc-vapor pressure. But, that means that, at the temperature T_2 , the activity curve from the point C on, by way of B to the point A, will have to run parallel to the abscissa; at the temperature T_2 , all concentrations between z and y will have the same activity values. The vapor pressure, and thereby the activity, will be determined here—as it is usual in the bi-phase region—by the phase that is more volatile. In case no dissociation has taken place, the activity value determined by the point M would correspond to the alloy

having a composition of x . But, the dissociation increases this activity value by an amount that is determined by the distance B-M. An increase of the activity, however, is equivalent to an increase of the vapor pressure of the volatile component. And, as a matter of fact, the vapor pressure is as high as that of a molten mass having a composition of x . Accordingly, in each case, the vapor pressure of the molten mass, which at a given temperature is in a state of equilibrium with the mixed crystal, will have to be the determining factor for the absolute magnitude of the vapor pressure in the biphasic area (molten mass + mixed crystal). When the temperature is lowered further, to T_1 , then a homogeneous mixed crystal will be formed with the originally assumed concentration of x , after passing the solidus line. When we assume once more, for the sake of simplicity, that in the case of this temperature, too, no essential change of the activity will take place in relation to the temperature T_2 , then the result for this temperature will have to be a vapor pressure the value of which will be determined solely by the temperature coefficient of the vapor pressure, when we consider the melting heat at the same time.

On the basis of these general considerations, the course of the vapor pressure curves in the biphasic area (molten mass—mixed crystal rich in aluminium) can be interpreted easily: after the passage of the liquidus line, we shall find an increase of the vapor pressure that is dependent on the concentration of the given alloy and that may be more or less important; in the case of alloys rich in Al, it will lead to the formation of a maximum (5 and 10% of zinc per weight). In the case of alloys rich in Al, this maximum will have to come about in the following way: After the passage of the liquidus line, two tendencies working in opposite directions will become effective: 1. The lowering of the temperature has the effect of decreasing the pressure, while 2. when the temperature goes down, the intensity of the dissociation, i.e., the enrichment of the molten mass with zinc, has the effect—immediately below the liquidus line—of increasing the pressure.

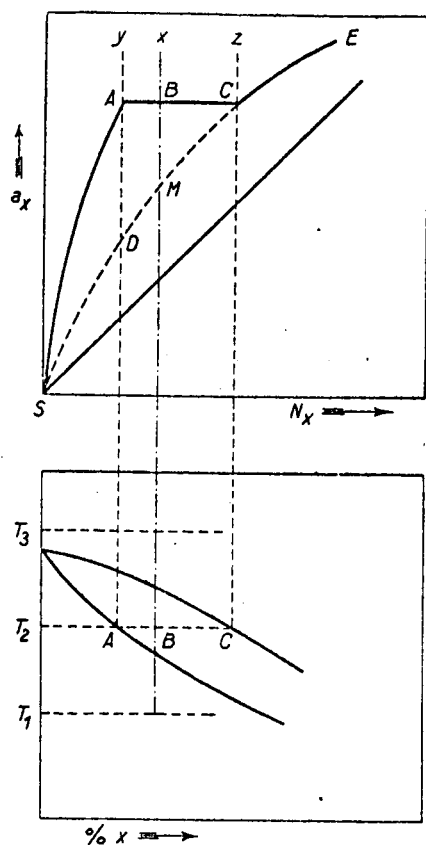


Fig. 6

Activity in the biphase region of molten mass and mixed crystal.

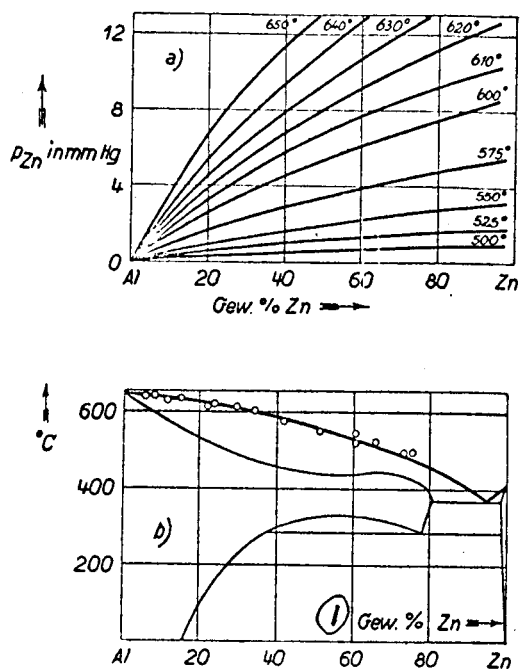


Fig. 7

Plotting of the liquidus line on the basis of vapor pressure measurements. [1% Zn per weight]

When, after the solidus line has been passed, an alloy having the initial concentration appears once more in the form of a homogeneous mixed crystal, then this process, which reverses the dissociation into a molten mass that is richer in zinc, and into a mixed crystal that is poorer in zinc, will bring about, in a discontinuous manner, a downward trend of the zinc-vapor pressure. As the figures show, the experimental findings are in complete agreement with the preceding theoretical considerations.

Fig. 7 may serve as a quantitative proof of the correctness of the above derivation for the course of the vapor pressure curves in the biphase region. In Fig. 7, the construction of the liquidus line of the system Al-Zn from the experimentally determined vapor pressure values of various alloys within the biphase

region has been represented. The values used in the determination of the liquidus line have been found in the following way: The vapor pressure values that pertain to the individual concentrations were read from the $\log p$ - $1/T$ -diagrams for homogeneous molten masses between 500 and 650° C—partly by means of extrapolation. With their aid, we plotted the isothermal lines as shown in Fig. 7a by 10° steps. When we take the pertinent vapor pressure values from the vapor pressure curves that have been determined experimentally within the biphasic region for certain temperatures, then the pertinent concentrations can be read from the isothermic lines of Fig. 7a. These values will have to belong—in accordance with the considerations based on Fig. 6—to the temperatures of the liquidus line for these very concentrations. For the construction, we made use of the vapor pressure curves of alloys having 5, 10, 30, and 55% of zinc, per weight. The agreement of the temperatures of the liquidus line as found in this way with the values as discovered by means of thermic analysis¹⁾ (Fig. 7b) is very satisfactory.

The conditions in the homogeneous molten masses of the Al-Zn alloys have been summarized once more in Fig. 8, on the basis of the measurements performed. The measuring values have been shown solely for the molten state, in the form of a $\log p$ - $1/T$ -diagram. The vapor pressure curves are practically parallel for all concentrations examined, i.e., the vaporization heat of zinc is independent of the quantity of the aluminium added to the alloy. In Table I, we have compiled the values of the zinc vapor pressures of the alloys investigated, in the form of a numerical tabulation, for 3 different temperatures. In Table 2, Column 2, the λ -values as calculated according to Clausius-Clapeyron have been presented in the form of a numerical tabulation. We may conclude from the constancy of the vaporization heat that the partial mixing heat is but slightly different from zero.

1) Cf. A. Burkhardt, Technologie der Zinklegierungen, II. Ed., Berlin, 1940, pp. 4-5, contains bibliography.

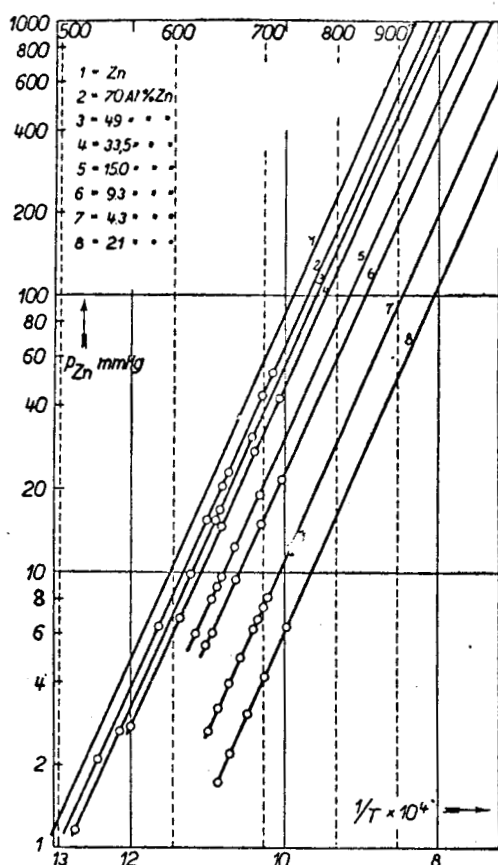


Fig. 8

Vapor pressures of
molten Al-Zn masses.

Table 1

Al-Zn. p_{Zn} -values in mm Hg.

Atom-% Zn	100	70,0	49,0	33,5	15,0	9,34	4,38	2,12
650°	26,0	20,2	17,2	14,2	9,25	6,65	3,35	1,86
725°	85,0	65,0	55,0	46,0	29,7	21,0	11,0	5,90
800°	235,0	182,0	153,0	125,0	80,5	57,5	29,5	16,1

Table 2

Al-Zn. Vaporization and
mixture heat figures.

Atom-%	100	70,0	49,0	33,5	15,0	9,3	4,4	2,1
λ in kcal								
650 bis	28,8 ₆	28,8 ₀	28,4 ₈	28,4 ₈	28,3 ₅	28,3 ₅	28,4 ₈	28,2
800°								
W_M^d								
725°	—	-0,05	-0,3 ₇	-0,3 ₇	-0,50	-0,50	-0,3 ₇	-0,6 ₅

The order of magnitude may be estimated at less than -0.5 kcal, and the endothermic nature of the mixing heat may be considered certain. The differences of the vaporization heat as measurements for the partial mixing heat $W_M^d = \lambda_{Leg} - \lambda_0$, Column 3 of Table 2, are within the limits of the measuring precision, which amount to some 2% of the absolute amounts of the vapor pressures.

The isotherms of the activity values (Table 3, Fig. 9) may be considered a further indication of the fact that the partial mixing heat is but small; they make it quite evident that here, too, an approximation to Raoult's straight line can be observed, in accordance with the theoretical requirements, as the temperature increases. The small negative mixing heat figures that correspond to the small temperature coefficient of the activity, might well be connected with the form of

the diagram of state of the Al-Zn system, within which no compound exists that will crystallize out of the molten flow. In view of the small temperature coefficient of the activity, we shall have to do without an indirect determination, by way of calculation, of the integral mixing heat figures on the basis of the temperature coefficient of the activity. As to sign and order of magnitude, the estimate of the maximum integral mixing heat at less than -0.5 kcal is in agreement with the maximum mixing heat of -1.0 kcal²⁾ as determined experimentally by M. Kawakami¹⁾.

Table 3

Values of the activities and of the changes of the free energy of Al-Zn-alloys.

Atom-% Zn	P_{Zn} mm Hg	$\frac{P}{P_0} = a_{Zn}$	$\frac{a}{N} = f_{Zn}$	$-RT \ln a_{Zn}$ cal
650°				
100,0	26,00	1,00	1,00	$\pm 0,00$
70,0	20,20	0,77 ₇	1,11 ₀	+ 465
49,0	17,20	0,66 ₂	1,35 ₀	+ 755
33,5	14,25	0,54 ₈	1,63 ₅	+1060
15,0	9,25	0,35 ₅	2,36 ₀	+1900
9,34	6,65	0,26 ₀	2,79 ₀	+2470
4,38	3,35	0,12 ₈	2,92 ₄	+3775
2,12	1,86	0,071	3,32 ₄	+4850
800°				
100,0	235,0	1,00	1,00	$\pm 0,00$
70,0	182,0	0,77 ₄	1,10 ₆	+ 550
49,0	153,0	0,65 ₁	1,32 ₈	+ 912
33,5	125,0	0,53 ₂	1,58 ₀	+1345
15,0	80,5	0,34 ₂	2,28 ₀	+2290
9,34	57,5	0,24 ₀	2,57 ₀	+3050
4,38	29,5	0,12 ₅	2,85 ₅	+4440
2,12	16,1	0,06 ₅	3,18 ₇	+5700

In Fig. 10, the measuring results of the activity coefficients as dependent on the atomic refraction have been presented. The deviations from Raoult's Law, that find their expression in the curve of the activity coefficients, present the curve that is to be expected, according to the theory (Fig. 10). It is of interest, however, that the temperature coefficient of the a/N -values is considerably smaller than in the Al-Mg system. This is a finding, on the basis of which only a small

1) M. Kawakami, Science Rep. Tohoku Imp. Univ. 19, 521 (1930).

2) In view of the great precision of the present vapor determinations, we believe, however, that we may be permitted to attribute lesser importance to the data obtained by M. Kawakami.

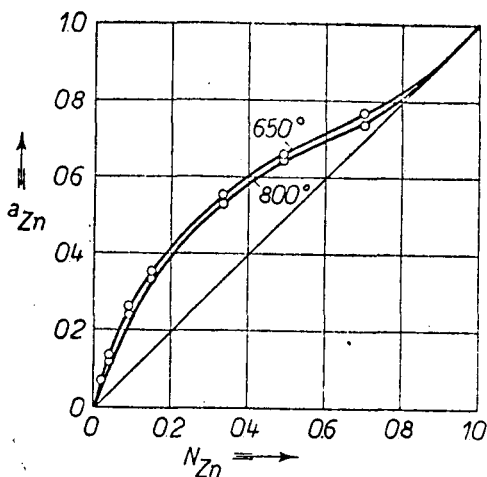


Fig. 9

Al-Zn. Activity isotherms.

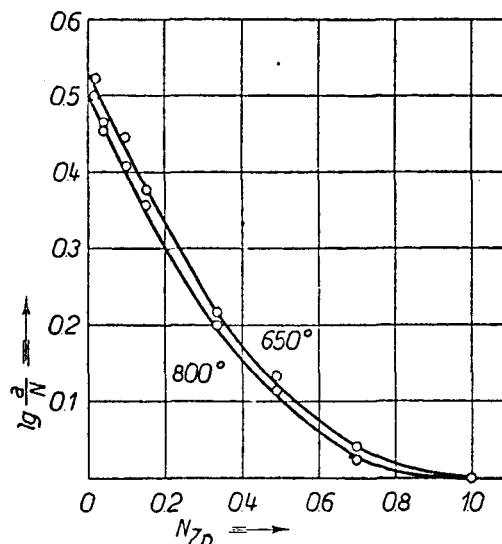


Fig. 10

Al-Zn. Deviation from Raoult's Law.

integral mixing heat can be assumed. The progress of the values for the changes of the free energy (partial residual molar work) presents a curve (Table 3, Column 5) that corresponds to the thermodynamic postulates.

The $\log a/N$ -curves show a course that is analogous to the lead-cadmium and thallium-tin systems¹⁾. It was obvious, therefore, to examine whether the molten Al-Zn-masses investigated also represent regular concentrated mixtures, in the sense of the definition given by J. H. Hildebrand²⁾. For them, the following equation will have to apply:

$$\log \frac{a_1}{N_1} = \beta \cdot N_2^2,$$

when β is a temperature independent constant. When we examine the results found for the Al-Zn system, then we shall obtain for β a value of some 0.5 as shown by Table 4.

1) J. H. Hildebrand and N. J. Sharma, Journ. Amer. Chem. Soc. 51, 462 (1929).

2) Cf. K. Jellinek, Lehrbuch der physikalischen Chemie, vol. IV, p. 472 ff.

Table 4

Atom-%	100	70,0	49,0	33,5	15,0	9,34	4,38	2,12
β_{650°	—	0,5 ₀	0,5 ₀	0,4 ₈	0,5 ₂	0,5 ₃	0,5 ₁	0,5 ₄
β_{800°	—	0,4 ₉	0,4 ₇	0,4 ₅	0,5 ₀	0,5 ₀	0,5 ₀	0,5 ₂

The constancy of the values of β for temperatures between 650 and 800° C is so good that the molten masses in the Al-Zn system may be designated, with high approximation, as regular concentrated mixes.

c) Discussion of the experimental results.

When we judge the course of activity curves, particularly for molten systems, then it is possible to have, kinetically, a clear quantitative picture of how they come into existence¹⁾. When A and B are the two components of the mixture, then forces are interacting between them, the size of which depends on the temperature. When the forces interacting between A and B are of the same size as the ones interacting between A and A or B and B, in the case of the presence of the pure components, then the lowering of the vapor pressure of the volatile solvent will follow the laws of the diluted solutions, i.e., the activity values p/p_0 will be located on the straight line of Raoult. In this case, we have assumed, for the sake of simplicity, that the forces of the pure components that are interacting between A and A or between B and B, have the same value. But, if the forces of attraction that are interacting between A and B are larger, then the consequence thereof will be that the energy that will have to be brought in for the vaporization process will be larger than the one needed in the case of the pure substances. This means that the lowering of the vapor pressure of the volatile solvent is larger than is postulated on the basis of Raoult's equation $p/p_0 = N$. The state of the solution is mirrored, within the activity curves, by a curve that takes its course below

1) Cf. K. Jellinek, Lehrbuch der physikalischen Chemie, Stuttgart 1933, vol IV, p. 480 ff.

Raoult's straight line ("negative" activity curves). If any repulsive forces exist between the particles of the solvent and the particles of the dissolved substance, then we shall obtain "positive" activity curves, in which the a -values are located above Raoult's straight line. In the extreme case, if the two components were incapable of mixing with one another, then this curve would have to be a straight line that would take its course from the activity value 1 and run parallel to the abscissa. As to the examination of the energetic state of molten alloy masses, the question is of interest, to what extent the compounds that are crystallizing out of the molten flow, are possibly still present as such or dissociated in the molten flow¹⁾. Due to the absence of any experimental data, that might be able to support the hypothesis of the presence of more or less thoroughly "dissociated" compounds in molten alloy masses, it appears advisable, for the time being, to collect material on the course of the activity isotherms for the molten state.

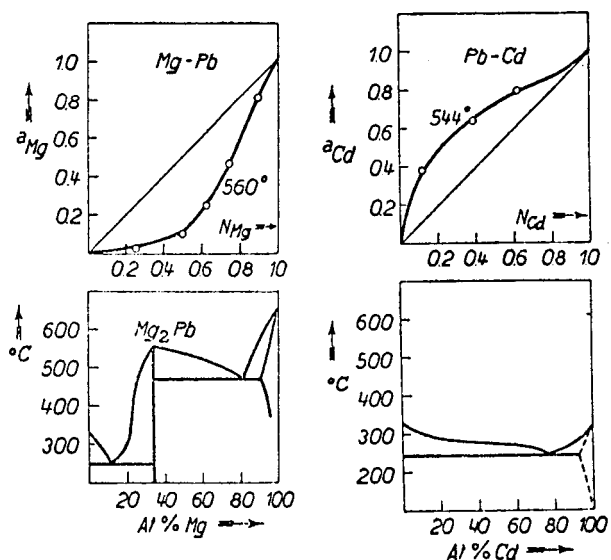


Fig. 11

Activities of Mg-Pb alloys and of Cd-Pb-alloys
(according to C. Wagner and K. Jellinek).

¹⁾ F. Dolezalek, Ztschr. physikal. Chem. 64, 727 (1908), 71, 191 (1910), 83, 40 (1913), 93, 585 (1919), 94, 72 (1919), 98, 395 (1921).

When we compare the activity curves that have been found up to this time by the use of various methods, with the diagrams of state of the binary alloys, then it will seem to us that the form and position of the activity curves are connected with the curves of the liquidus lines. This hypothesis has been represented by Fig. 11. In this Figure, the activity curves of the Mg-Pb and Cd-Pb systems have been reproduced, together with the pertinent diagrams of state. In the Mg-Pb system, C. Wagner and G. Engelhardt¹⁾ have observed a very pronounced negative activity curve. It does not appear unjustified to connect this very considerable deviation of the activity values from Raoult's straight line with the character of the intermetallic combination Mg_2Pb which originated in the fused mass. As it has been demonstrated by E. Zintl and H. Kaiser²⁾, Mg_2Pb crystallizes according to the fluorite pattern. According to Zintl, the crystallo-chemical delimitation of the elements that are 1 to 4 places ahead of the rare gases, from those elements that are 5 to 7 places ahead of them, is particularly clearly visible in the case of magnesium alloys. The pronounced hetero-polarity of the compound Mg_2Pb evidently finds its expression in the extraordinarily strong negative character of the activity curve.

On the other hand, when we compare to it the activity curve of the Pb-Cd system, which has been determined by K. Jellinek and G. A. Rosner³⁾, then the difference from the Mg-Pb system is clearly visible. Cadmium and lead form a eutectoid system with a temperature that lies but a mere 100° C below the melting points of the components. Despite the fact that the experimental temperature of 445° C as chosen by K. Jellinek lies some 200° C above the liquidus line, the activity curve presents a strongly positive character. It does not appear impossible that this fact is connected with the observation that lead in metallic systems

1) C. Wagner and G. Engelhardt, Ztschr. physikal. Chem. A 159, 241 (1932).

2) E. Zintl and H. Kaiser, Ztschr. anorgan. allg. Chem. 211, 113 (1933).

3) K. Jellinek and G. A. Rosner, Ztschr. physikal. Chem. A 152, 67 (1931).

(Cu-Pb, Al-Pb, Zn-Pb) has a tendency toward being immiscible. The same thing is true of the conditions found, according to the two communications mentioned, for molten Al-Mg and Al-Zn alloys: the negative course of the activity curve in the Al-Mg system might be connected with the intermetallic compounds that come into existence when the molten masses of medium concentrations solidify; one of these, Al_2Mg_3 , is supposed to have a partly heteropolar character, according to U. Dehlinger¹⁾. On the other hand, no compound will crystallize out of molten Al-Zn masses: the activity curve presents a "positive" character.

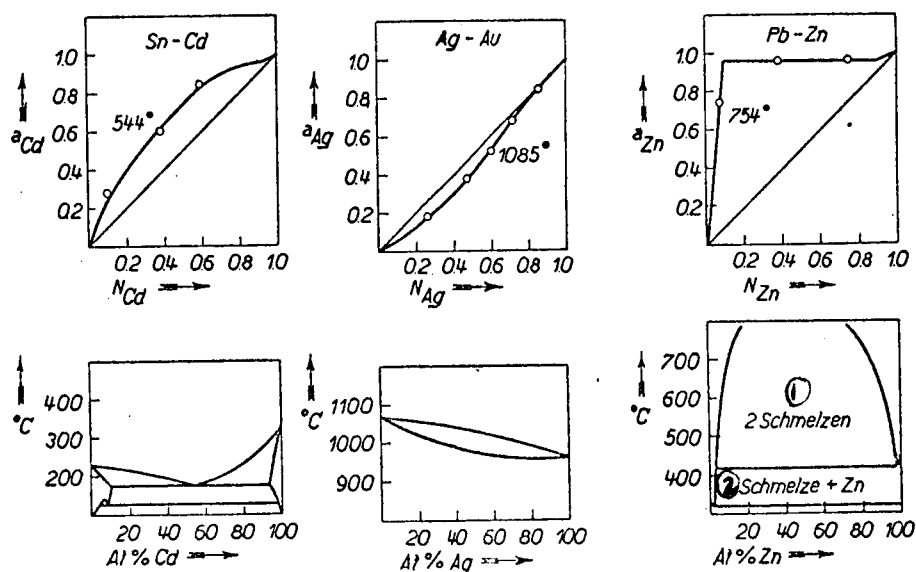


Fig. 12

Activities and diagrams of state for alloys of Sn-Cd, Ag-Au, and Pb-Zn (according to C. Wagner and K. Jellinek).
 [① 2 molten masses ② molten mass + Zn]

In Figs. 12 and 13, the measuring results obtained on other systems on the basis of measurements performed by C. Wagner or K. Jellinek have been compiled, in the same manner of presentation. It may be seen clearly that the above hypothesis of the connection between the form and the position of the activity curve on the

¹⁾ U. Dehlinger, Ztschr. Elektrochem. 46, 627 (1940).

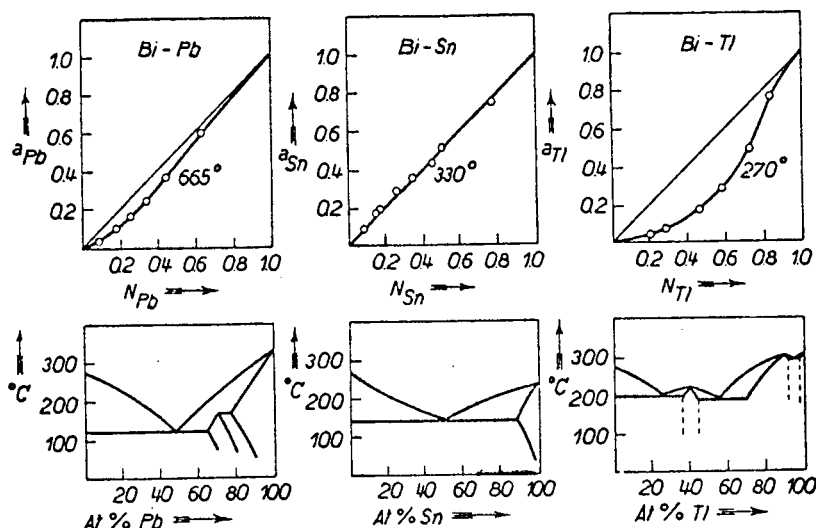


Fig. 13

Activity values and diagrams of state of alloys of Bi-Pb, Bi-Sn, and Bi-Tl (according to C. Wagner and Engelhardt).

one hand, and the curve of the liquidus line on the other hand, may be transferred to these systems without any constraint. As to a quantitative evaluation of this situation, the theoretical bases are not yet available at this time.

In any case, there is not as yet any experimental intimation of the existence—assumed occasionally—of intermetallic compounds in the fusible mass so that it appears that the concept of "dissociation" also cannot be applied simply to molten alloys. E.g., F. Dolezak has established a theory to the effect that any deviation of the activity values from Raoult's Law points to a chemical reaction: negative a -curves are supposed to suggest the formation of a compound, while positive ones are supposed to indicate that the pure components are associated and will dissociate when mixed. K. Jellinek¹⁾ has pointed out justly that the assumption of van-der-Waals forces alone is perfectly sufficient to explain positive and negative activity curves, just as we do not talk of chemical reactions when we consider the deviations of the behavior of real gases from the ideal law of gases. Experimental data

1) K. Jellinek, Lehrbuch der physikalischen Chemie, Stuttgart 1933, vol. IV, p. 484 ff.

actually speak strongly against the ideas of F. Dolezalek: e.g., the fact that mixtures of liquid nitrogen and argon present positive activity curves¹⁾. The same statement applies to a few tested series of molten alloy masses (e.g., Pb-Cd)²⁾ or, as it has been shown in this paper, to Al-Zn). But the hypothesis that in these cases (particularly in the case of argon) an association of the unmixed components is present, seems hardly defensible³⁾.

For that reason, it might be simpler to describe the energetic state of molten alloy masses qualitatively in the kinetic manner as suggested above, and qualitatively by the use of the activity values. The experiences gathered up to this time, inasmuch as formation temperatures and mixing temperatures are concerned, may be fitted into this concept, without any constraint. Moreover, e.g., the high melting maxima that are characteristic for intermetallic compounds having a heteropolar structure and high formation temperatures (Mg_2Pb , Mg_3Sb_3 and other ones) may be interpreted in the following way: the forces of attraction which find their expression in the "negative" activity curves, show already such a strong effect at very high temperatures⁴⁾ that a crystallization of the compounds out of the molten mass will already take place at these temperatures.

It appears, therefore, to be a rewarding task of experimental research to gather further experimental material, particularly by using a systematic approach. The alloys of magnesium and of the alkali metals which have been tested particularly by E. Zintl, will appear in the foreground, in this connection, inasmuch as the

1) K. Jellinek, *ibid*, p. 485.

2) K. Jellinek and G. A. Rosner, *Ztschr. physikal. Chem. A* 152, 67 (1931).

3) K. Hauffe and C. Wagner, *Ztschr. Elektrochem.* 46, 160 (1940) stress, also in view of the fact that typical coordination grids are present in solid intermetallic compounds, that the concept of the molecule is not applicable to the liquid phase in alloy systems.

4) I.e., at temperatures that are sufficiently high above the liquidus line, so that one would have to assume, in the case of the absence of stronger forces of attraction, that the molten masses are already very close to the state of the ideal concentrated mixtures.

crystallo-chemical delimitation of the parts of the alloys is concerned, which is especially clear in their case.

Summary

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The vapor pressures of zinc over Al-Zn alloys of the entire concentration range were determined by means of a method that is based on the principle of the dew-point, and which has been described in detail. The measuring results were used for the calculation of the activities, of the free energy, and of the vaporization temperatures. The Al-Zn molten masses were shown to be regular concentrated mixtures.

The results were discussed, with an eye toward the possible connections between the form of the activity curves and the liquidus lines of binary molten metal mixtures.

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